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Improved Model for Diffusion-Limited Current in Organic Metal-Insulator-Metal Diodes

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Abstract:

The analytic J-V formula for organic diodes recently derived by Bruyn et al. [2] is improved by considering electric field dependence of mobility. The improved formula is applied to four devices. The results calculated from original formula cannot arrive at good agreement with experimental data. The results calculated from the improved analytic formula are in good agreement with the complete numerical solutions, and both agree with experimental data very good.

Keywords: organic diode, non-symmetric barriers,

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1. Introduction

Because of the promise of low-cost and large-area electronic applications, organic semiconductors are the object of intense investigation [1-7]. The current in metal-insulator-metal (MIM) organic diode is space charge limited (SCL). It can be described by solving Poisson and drift-diffusion equations simultaneously by using some formulae of mobility. And these equations are difficult to analytically solve even taking mobility as a constant. So in long times, the SCL current was described by using the analytic Mott-Gurney formulae at high bias voltages with the diffusion current being negligible.

But at low and middle voltages, the diffusion current cannot be neglected. And in many works the diffusion-limited current in organic MIM diodes has been analyzed using the classical Shockley diode equation [1], $J = J_0[\exp(qV/\eta kT) - 1]$. Recently, Bruyn et al. [2] pointed out that the Shockley equation was derived to describe a bipolar current through a p-n diode, where the ideality factor is strictly related to the order of recombination. Applying this equation to unipolar devices with undoped semiconductors is therefore questionable. They [2] derived an analytical equation that describes the diffusion current for undoped semiconductors or insulators in MIM diodes with asymmetric contacts. This can substantially improve the accuracy of analysis of experimental data and charge-transport measurements in organic-semiconductor diodes. However, we notice that the mobility has been taken as constant in derivations of Bruyn et al. [2], so the resulting formulae is unsuitable for wide voltage ranges, and even for low and middle voltages the errors are non-negligible.

The traps have been recognized an important issue for SCL current characteristics to transport models [3-20]. There are two types of models to consider trap effects in literature. The first type of models separate all carriers into free and trapped [3-10], two representative methods are the mobility edge (ME) model [3-7] and trapped carrier model [8-10]. The second type of models treats all carriers as mobile [11-18], the trap effects are considered by treating the mobility of carriers as a function of electric field or density of carriers. Two representative methods are the exponential model of Pai [11-14], and the unified model of Pasveer [16] et al. The exponential model of Pai [11] has ever been an empirical model. However, Dunlap et al. [12] analytically derived the expression of mobility for organic semiconductors, confirmed the exponential model of Pai [11]. Subsequently, Blom et al. [14] proposed temperature dependent expressions for parameters in the exponential

model. Pasveer *et al*. [15] formulated the mobility as a function of temperature, density of charge carriers and electric field, and the model has been applied to many materials [15-18].

In one of our recent work [19], we consider non-symmetric barriers at contacts in the models of Pai [11] and Pasveer *et al*. [15] and applied them to single-crystal rubrene organic semiconductor. Our results [19] show that the exponential mobility model [11-14] can well describe current-voltage (J-V) data of single-crystal rubrene, the extracted parameters show correct temperature dependence, and the extracted barriers are non-symmetric. However, the model of Pasveer et al. [15] fails to fit J-V curves, and some parameters show inconsistent temperature dependence which should be constants in the theoretical framework of Pasveer et al. If comparing the model of Bruyn et al. [2] with model in [11-14, 19], it can be seen that the basic physical model of Bruyn et al. [2] can be included in [19] as special case. Since the exponential mobility model [11-14, 19] gives good description for typical diodes, and the analytic J-V formulae are very important and convenient for device modeling and analysis of experimental data, it is necessary to improve the analytic JV formulae by using exponential mobility model [11-14, 19].

2. Outline of fundamental formulae

The Poisson equation for description of the SCL current is as follows [3-19]

$$\frac{d^2\varphi}{dx^2} = -\frac{q}{\varepsilon_r \varepsilon_0} p(x) \tag{1}$$

for electric potential φ or field. Where x is the coordination, q is the elementary charge, p is density of holes; ε_0 is the free-space permittivity, ε_r is the dielectric constant of the semiconductor. The drift-diffusion equation for current J is as follows:

$$J(x) = -q\mu_p(x)p(x)\frac{\partial\varphi}{\partial x} - kT\mu_p(x)\frac{\partial p(x)}{\partial x} \tag{2}$$

Where μ_p is the mobility of holes. Assuming the thickness of organic layer is L, the left-side contact ($x = 0$) can be seen as Ohmic with low potential barrier W_{left}. And the right-side contact ($x = L$) can be seen as Schottky with high potential barrier W_{right}. $V_{bi}=W_{right}-W_{left}$ is the built potential. The boundary conditions used in solving procedure can be expressed as follows [2, 10, 19]: $p(0) = N_f \exp(-W_{left}/kT)$, $p(L) = N_f \exp(-W_{right}/kT)$;

$\varphi(0) = W_{left} + V$, $\varphi(L) = W_{right}$; $V - V_{bi} = \varphi(0) - \varphi(L)$. Bruyn et al. [2] used different notations for potential barriers: $\varphi_b = W_{right}$, $b = W_{left}$.

The numerical solutions of Eqs. (1-5) and Eq. (6) are troublesome. In order to derive an analytic solution, Bruyn et al. [2] proposed following analytic linear approximation for the Poisson equation (1)

$$\varphi(x) = V + b + (V_{bi} - V)(x/L) \tag{3}$$

We notice that the electric field evaluated from Eq. (3) is a constant being independent to coordinate

$$F = -\partial\varphi(x)/\partial x = (V - V_{bi})/L \tag{4}$$

The exponential mobility model of Pai [11] has been rationalized by Dunlap et al. [12] and has following form

$$\mu_p(F) = \mu_p(0)\exp\left(\gamma\sqrt{F}\right) \tag{5}$$

Where $\mu_p(0)$ and γ are two parameters, F is the electric field. If substituting Eq. (4) into Eq. (5), the mobility also is independent to coordinate. And the solving procedure in [2] can be directly apply to this case, then the analytic JV formula [2] can be improved to following form

$$J_p = \frac{qN_f\mu_p(0)(V - V_{bi})[\exp(qV/kT) - 1]\exp\left[\gamma\sqrt{(V - V_{bi})/L}\right]}{L\exp(qb/kT)[\exp(qV/kT) - \exp(qV_{bi}/kT)]} \tag{6}$$

As γ takes zero value, Eq. (6) would reduce to the formula of Bruyn et al. [2]

Although the mechanism of electric conduction is not thoroughly determined, the Gaussian model [3-19] for DOS has been recognized: $D(E) = \left(N_0/\sigma\sqrt{2\pi}\right)\exp\left[-(E - E_v)^2/2\sigma^2\right]$, where N_0, E_v, and σ are the total number of states, the center energy and the standard deviation of the Gaussian distribution, respectively. Assuming organic semiconductors are non-degenerate, the density of holes can be derived as [10, 19], $p = N_f\exp\left[-q\varphi(x)/kT\right]$, with effective DOS defined as

$$N_f = N_0\exp[(E_v - E_F)/kT]\exp\left[\sigma^2/2(kT)^2\right] \tag{7}$$

The coefficient $\mu_p(0)$ in Eq. (5) denotes the mobility at zero field. Blom et al. [14] observed a thermally activated behavior

$$\mu_p(0) = \mu_0\exp(-\Delta/k_BT) \tag{8}$$

They also demonstrated the linear dependence between γ and $1/T$, as following

$$\gamma = B(\frac{1}{k_B T} - \frac{1}{k_B T_0}) \tag{9}$$

This empirical dependence of γ on T has originally been proposed by Gill [13].

3. Results and discussions

We apply Eq. (6) based on the modified exponential model [11-14, 19] to four different polymers: poly[4'-(3,7-dimethyloctyloxy)-1,1' -biphenylene-2,5-vinylene] (NRS-PPV) [15], poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene) (OC_1C_{10}-PPV) [15], poly(3-hexylthiophene) (P3HT) [20], and Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene) (MEH-PPV) [8, 9], with their thickness of layer 560, 275, 95 and 270 nm, respectively. We calculate J-V curves from both analytic Eq. (6) and numerical solutions of Eqs. (1, 2). The theoretical results are compared with experimental data in Fig. 1.

The figure shows that the agreement of theoretical curves with experimental points is fairly good; covering all ranges of voltages involved and temperatures. However, the difference between results from analytic Eq. (6) and numerical solutions of Eqs. (1, 2) is very small and invisible in Fig. 1. Thus the analytic formula Eq. (6) is a good approximation to numerical solutions of Eqs. (1, 2). If one only wants J-V curves, it is enough to adopt Eq. (6); it is no longer to numerically solve Eqs. (1, 2).

In Fig. 1, we also plot the results as parameter γ in Eq. (6) taking zero values. It can be seen that the calculated curves in this situation would dramatically deviate from the experimental points. We also made a try to fit experimental data keeping γ as zero, but it is impossible to arrive at good fittings for J-V data at low and high voltage regions at same time. So it is necessary to make the modification in Eq. (6) with non-zero γ.

In Table 1, we list potential barriers and values of N_0, E_{vF} and σ for N_f. The table shows that the values of W_{right} always are larger than W_{left}, such asymmetric potential barriers imply positive built potentials. The table also shows that the values of σ in the range (0.08~0.11) eV are reasonable. The $E_{vF} = (E_v - E_F)$ always takes negative values. This implies that the Fermi energy always is higher than the energy level of valence, and the

non-degenerate assumption used in Eq. (2) for organic semiconductors is reasonable. In Fig. 2 we plot variation of N_f with temperature and smoothed curves by using Eq. (7), both agree with each other very good.

In Figs. 3 and 4, we plot variation of parameters $\mu_p(0)$ and γ with temperature, and curves smoothed by using Eqs. (8, 9). The two figures show that Eqs. (8, 9) can fit the data points very good. So the analytic J-V formula in Eq. (6) with expressions for parameters in Eqs. (8-9) are simple and sound tool for organic diodes. In Figs. 5, we plot percentage errors of smoothed values of N_f, $\mu_p(0)$ and γ relative to values in Table 1. The figure shows that the errors for N_f and γ are always very small, the fitting quality of smoothed curves are fairly good. As for $\mu_p(0)$ the fitting quality is fairly good for two materials NRS-PPV and OC_1C_{10}-PPV, merely for other two materials, P3HT and MEH-PPV, the errors are slightly large. Overall speaking, the fitting quality of smoothed values of N_f, $\mu_p(0)$ and γ is satisfactory.

4. Conclusion

In this paper, the electric field dependence of mobility for organic semiconductors is introduced in analytic J-V formula recently proposed by Bruyn et al. [2], and the modified formula is applied to four devices. The results from original formula cannot arrive at good agreement with experimental data. The results from the improved analytic formula are in good agreement with the complete numerical solutions, and both agree with experimental data very good. The modification introduced in this work is necessary; the improved formula is more precise and convenient for applications.

Acknowledgments

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Table 1 Temperature-independent potential barriers and N_0, E_{vF} and σ for N_f in Eq. (7) for NRS, OCC, P3HT and MEH organic diodes.

Fig. 1 (color online) Comparison of calculated *J-V* curves by using modified model with experimental data [6, 8] for NRS-PPV, OC_1C_{10}-PPV [15], P3HT [20] and MEH-PPV [8, 9] diodes with 560, 275, 95 and 270 nm thickness of organic layer at different temperatures. (solid lines: $\gamma \neq 0$; dashed lines: $\gamma = 0$).

Fig. 2 (color online) Variations of $N_f(T)$ with temperature, lines are smoothed curves by using Eq. (7)

Fig. 3 (color online) Variations of $\mu_p(0)$ with temperature, lines are smoothed curves by using Eq. (8).

Fig. 4 (color online) Variations of $\gamma(T)$ with temperature, lines are smoothed curves by using Eq. (9).

Fig. 5 (color online) Relative errors of $N_f(T)$ (□), $\mu_p(0)$ (○), and $\gamma(T)$ (◊) smoothed by using Eqs. (7, 8, 9) at different temperature points.

Table 1

	NRS	OCC	P3HT	MEH
W_{left} (eV)	0.695	0.58	0.30	0.30
W_{right} (eV)	1.55	0.67	0.40	0.40
N_0 (m^{-3})	4.1634E27	1.5365E027	4.4E22	3.5066E21
E_{vF} (eV)	-0.3518	-0.4897	-0.3601	-0.3301
σ (eV)	0.0793	0.1118	0.11	0.098

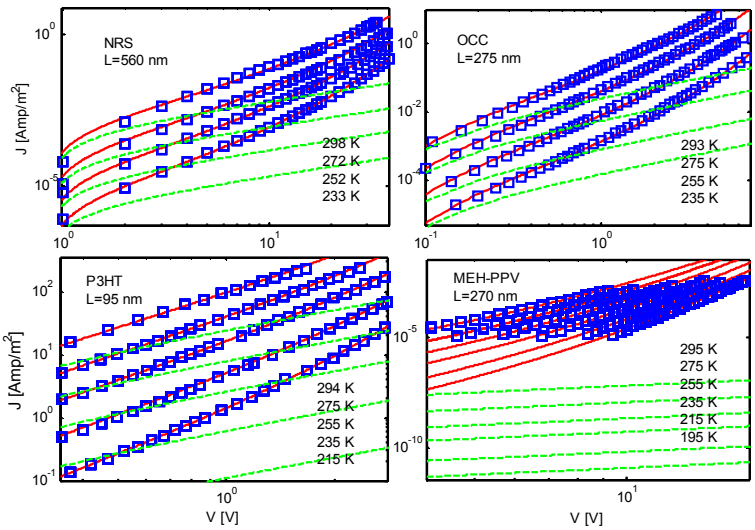

Fig. 1

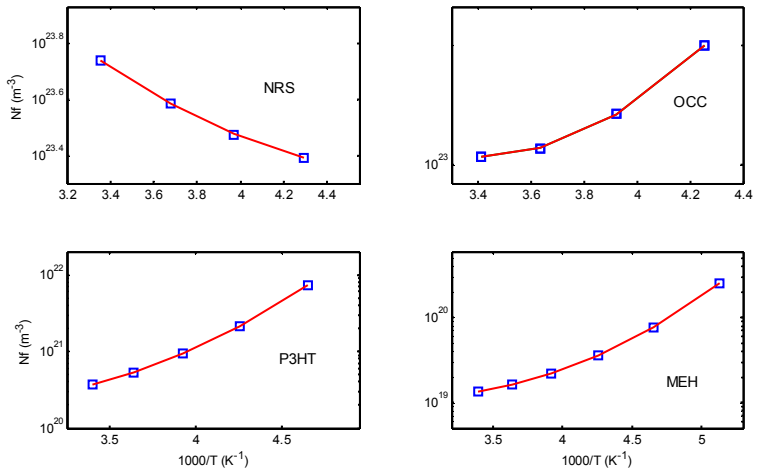

Fig. 2

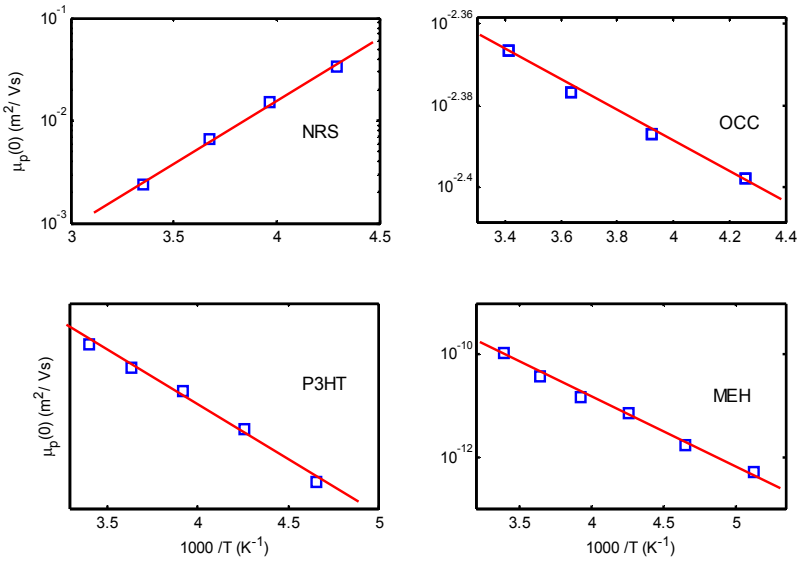

Fig. 3

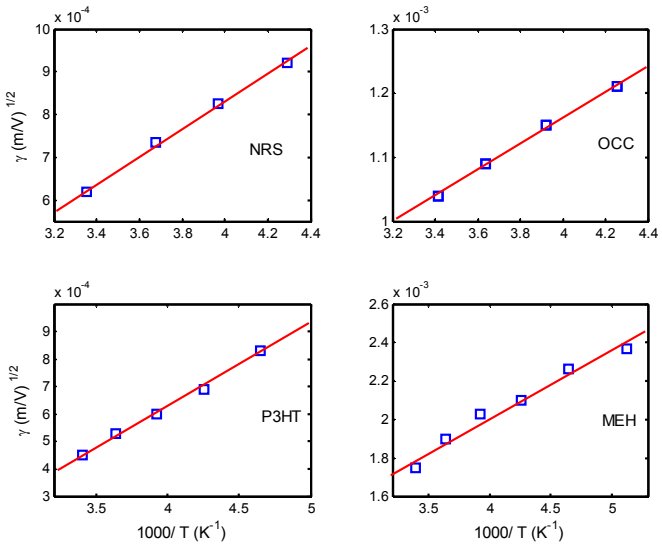

Fig. 4

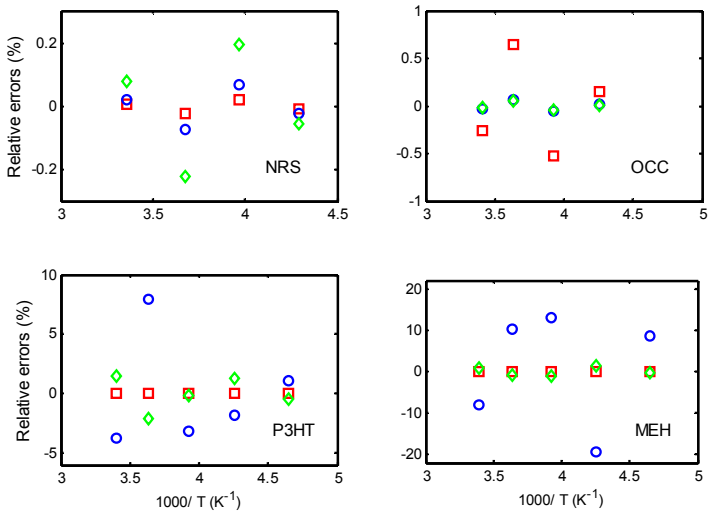

Fig. 5